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Date of request 10/12/95 Expected receipt of document 1 MONTH

Document number K-840 Date of document 12/28/51

Title and author (if document is unnumbered)

NON-IDEALITY OF URANIUM HEXAFLUORIDE VAPOR ; R.D. Ackley + D.W. Magnuson

(This section to be completed by Document Center)

Date request received 10/12/95

Date submitted to ADC NA

Date submitted to HSA Coordinator 10/12/95

(This section to be completed by HSA Coordinator)

Date submitted to CICO NA Publicly Available

Date received from CICO NA Through NTIS

Date submitted to ChemRisk/Shonka and DOE 11/28/95

(This section to be completed by ChemRisk/Shonka Research Associates, Inc.)

Date document received \_\_\_\_\_

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10252-C

Date of Issue: December 28, 1951

This document consists of 9 pages  
No. 8 of 8 copies, Series B.

Report Number: K-840 *AECD-3475\**

Subject Category: CHEMISTRY - GENERAL

NON-IDEALITY OF URANIUM HEXAFLUORIDE VAPOR

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### A B S T R A C T

The equation of state  $P(1 + AP)V = nRT$ , where  $A$  is a function of temperature but not of pressure, was assumed for uranium hexafluoride vapor up to a pressure of one atmosphere, and moderately accurate values of  $A$  for two temperatures were determined by a method based on P-V-T measurements. These values were  $0.032 \text{ atm.}^{-1}$  at  $60^{\circ}\text{C}$ . and  $0.021 \text{ atm.}^{-1}$  at  $94^{\circ}\text{C}$ . (Their standard deviations were  $0.003 \text{ atm.}^{-1}$  and  $0.002 \text{ atm.}^{-1}$ , respectively.) In order to confirm these results,  $A$  was determined at  $61.1^{\circ}\text{C}$ . by utilizing a microwave dielectric constant technique. The more precise value obtained, with its probable error, was  $(0.0330 \pm 0.0007) \text{ atm.}^{-1}$ .

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# NON-IDEALITY OF URANIUM HEXAFLUORIDE VAPOR

## PART I. NON-IDEALITY FROM P-V-T MEASUREMENTS

In the determination of certain uranium hexafluoride adsorption isotherms where the ratio of volume to surface was relatively large, it was observed that some of the isotherms exhibited negative hysteresis, a phenomenon which is contrary to experience. (Negative hysteresis refers to the desorption branch of the isotherm being below the adsorption branch.) The calculation of these isotherms was based on the assumption that uranium hexafluoride was an ideal gas since previous work had indicated that such an assumption was probably justifiable (1). However, since the negative hysteresis could be explained on the basis of non-ideality of uranium hexafluoride, a brief investigation of this aspect was carried out.

It follows from experiment and, also, from the van der Waals equation that the behavior of most gases at pressures of the order of one atmosphere may be represented by the equation  $P(1 + AP)V = nRT$ , where  $A$  is a function of temperature but not of pressure and the other terms have their usual significance. Therefore, to evaluate  $A$ , all that is necessary is to measure the pressures of a quantity of gas corresponding to two different known volumes under approximately isothermal conditions. This was done for uranium hexafluoride at 44°C., 60°C., and 94°C. The apparatus consisted essentially of two connecting volumes, along with temperature and pressure measuring devices, in an air thermostat. In addition, one of the volumes was connected to a vacuum line and a gas manifold. A more detailed description of the apparatus employed will appear in a forthcoming report by the writer concerning uranium hexafluoride adsorption. The number of individual determinations of  $A$  was four at 44°C. and three at each of the other two temperatures; also, the volume ratio of the two volumes together to one of them, the quantity actually used, was based on three determinations. The results of these measurements are summarized in table I.

TABLE I  
NON-IDEALITY OF URANIUM HEXAFLUORIDE AT VARIOUS TEMPERATURES

<u>Temperature, °C.</u>	<u>A, atm.<sup>-1</sup></u>	<u>Standard Deviation of A (s<sub>A</sub>), atm.<sup>-1</sup></u>
44	0.027	0.007
60	0.032	0.003
94	0.021	0.002

The principal reason for the lack of precision in the result for 44°C. is that the lower vapor pressure of uranium hexafluoride, at this temperature, limited this set of measurements to relatively low working pressures. Actually, it is to be expected that  $A$  for 44°C. would be somewhat greater than  $A$  for 60°C.

The extent of non-ideality described above satisfactorily explained the negative hysteresis.

## PART II. NON-IDEALITY FROM DIELECTRIC CONSTANT MEASUREMENTS

Recent dielectric constant measurements of uranium hexafluoride at 9400 mc./sec. (2,3) did not show any effects of non-ideality, but it was possible that the pressures used, less than 40 cm. Hg, were not large enough to detect these effects. It was deemed advisable to extend the measurements at 61.1°C. to higher pressures in order to confirm the results described in Part I, and possibly to obtain a more precise value of the parameter of non-ideality. The apparatus has been described in the above reports (2,3), in which frequency changes of a resonant cavity are used to calculate dielectric constants.

The dielectric constant,  $\epsilon$ , is related to the molecular density,  $n_m$ , and molecular polarizability,  $\alpha$ , by the equation

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4 \pi n_m \alpha}{3},$$

and variations of the quantity  $\frac{\epsilon - 1}{\epsilon + 2}$  with pressure can be used to detect non-ideality. The dielectric constant,  $\epsilon$ , can be calculated from the measured resonant frequencies when the cavity is evacuated and filled with dielectric,  $\gamma_0$  and  $\gamma$ . This equation is

$$\gamma^2 = \epsilon \gamma_0^2 \quad \text{or} \quad \epsilon - 1 = \frac{\gamma_0}{2\gamma} \left(1 + \frac{\gamma_0}{\gamma}\right) \frac{2\Delta\gamma}{\gamma_0}$$

The resonant frequency of the cavity was determined for zero pressure and for each of 13 pressures of uranium hexafluoride vapor for intervals of 4 to 6 cm. Hg. The maximum pressure was 73.11 cm. Hg and the temperature of the cavity was 61.1°C.

The  $\Delta\gamma$  values (the frequency shift from the evacuated cavity resonant frequency) were multiplied by the factor  $\frac{\gamma_0}{2\gamma} \left(1 + \frac{\gamma_0}{\gamma}\right)$  and an equation of the form

$$\frac{\gamma_0}{2\gamma} \left(1 + \frac{\gamma_0}{\gamma}\right) \Delta\gamma = a_1 P + a_2 P^2$$

was fitted to the data. The effect of the interaction of the dipoles, the  $\epsilon + 2$  term, cannot be neglected, thus a small correction must be applied to the value of  $a_2$ . This can be shown to be  $\frac{\Delta a_2}{a_1} = \frac{-(\epsilon - 1)a}{3} = -0.001147$

atm.<sup>-1</sup> in which  $(\epsilon - 1)a$  is the dielectric constant of uranium hexafluoride vapor per atmosphere.

The coefficient  $a_1$  and  $a_2$  were determined by grouping the data and solving for the best fit coefficients. These values were

$$a_1 = 0.208689 \frac{\text{mc./sec.}}{\text{cm. Hg}}$$

$$a_2 = 0.00009372 \frac{\text{mc./sec.}}{(\text{cm. Hg})^2}$$

$$\frac{a_2}{a_1} = 0.0004491 \text{ cm. Hg}^{-1} \text{ or } 0.03413 \text{ atm.}^{-1}$$

By comparison to the non-ideal gas equation  $P + AP^2 = \frac{nRT}{V}$  it is obvious that

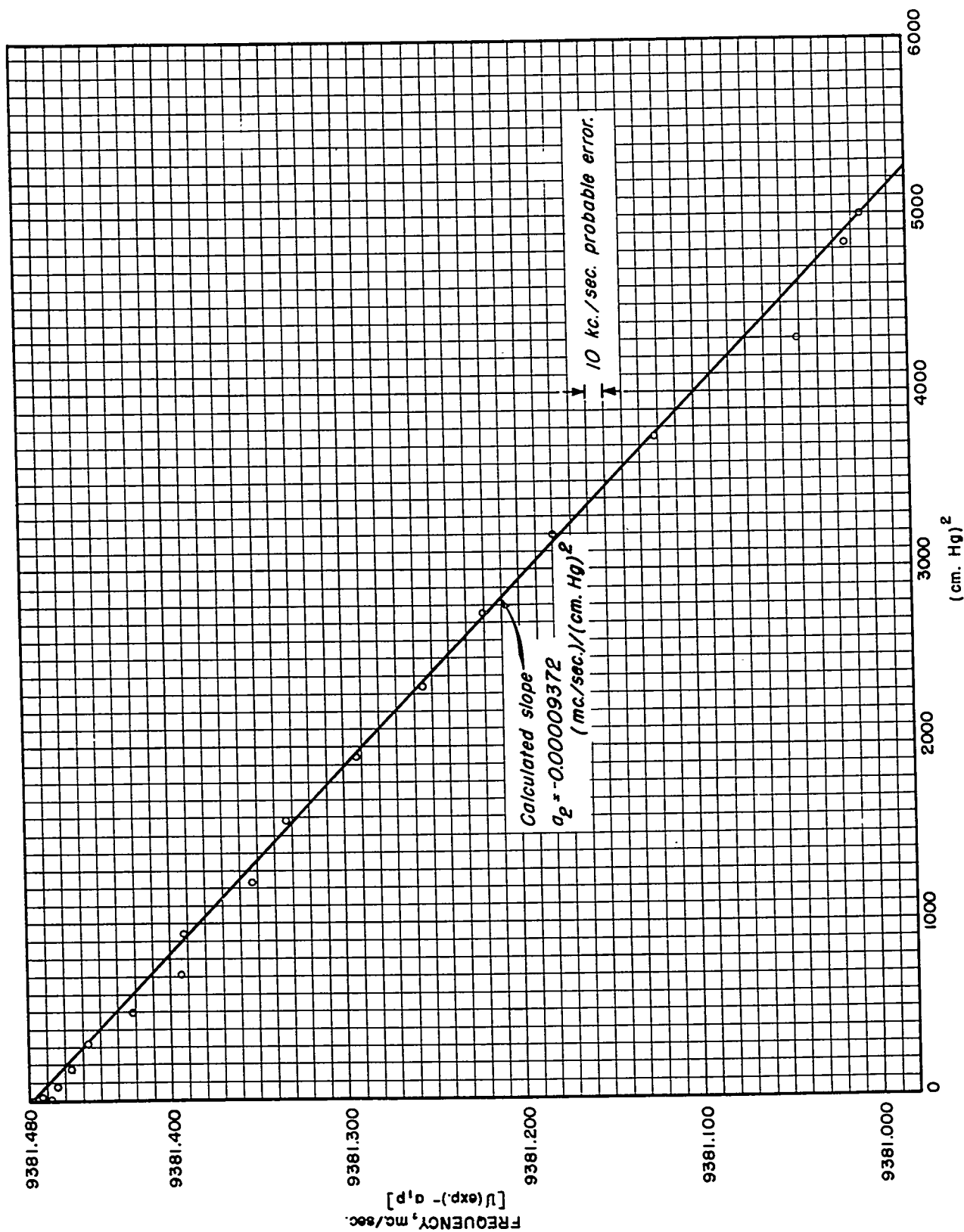
$$A = \frac{a_2 + \Delta a_2}{a_1} = 0.03298 \text{ atm.}^{-1}$$

The agreement between the experimental data and the derived curve is shown in Figure 1 in which the frequency ( $\nu - a_1P$ ) is plotted vs.  $(\text{cm. Hg})^2$ . The negative slope of this line is the coefficient  $a_2$ . Most of the experimental data lies within the 10 kc./sec. probable error of the apparatus as previously discussed (2,3). On this basis the slope was determined to 2% or

$$A = (0.0330 \pm 0.0007) \text{ atm.}^{-1}$$

The value of the dielectric constant of uranium hexafluoride corrected to standard conditions is  $\epsilon - 1 = 4133.2 \times 10^{-6}$  which is 1.6% smaller than the previous value,  $4202.2 \times 10^{-6}$ , obtained at this temperature. If the present data up to 30.70 cm. Hg are used to calculate the dielectric constant by means of least squares, then  $\epsilon - 1 = 4202.8 \times 10^{-6}$  which is only  $0.6 \times 10^{-6}$  higher than the previous value.

The purity of the uranium hexafluoride vapor was found to be better than 99.8% on material purified on a similar manner, and the comparison of the results indicate that the purity did not change.



NON IDEALITY OF URANIUM HEXAFLUORIDE VAPOR  
 FIGURE 1

## ACKNOWLEDGEMENT

The assistance of Mr. D. S. Hawthurst in the determination of the statistical quantities in part I is greatly appreciated.

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